On the Limitations of Breakthrough Curve Analysis in Fixed-Bed Adsorption

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Knox, J. C.; Ebner, A. D.; LeVan, M. D.; Coker, R. F.; Ritter, J. A., Limitations of Breakthrough Curve Analysis in Fixed-Bed Adsorption. *Ind Eng Chem Res* **2016**.

Introduction

- Fixed Beds used for Separation via Gas Adsorption in Numerous Applications, for example:
  - Chemical processing industry (petrochemicals, foods, medicines, etc.)
  - Thermochemical energy storage
  - DOE funded efforts to develop affordable flue gas CO_2 capture systems
  - Atmospheric control in habitable volumes
- Generally multiple bed cyclic processes such as pressure swing adsorption (PSA) or temperature swing adsorption (TSA)
- Direct simulation of the highly random sorbent particle packing and small-scale features of the flow between particles in a fixed-bed is CPU intensive
- To achieve cyclic steady-state in a process simulation, as required for process design, 1-D models are utilized

Fluid flow in a packed bed – studies in catalyst reactor design

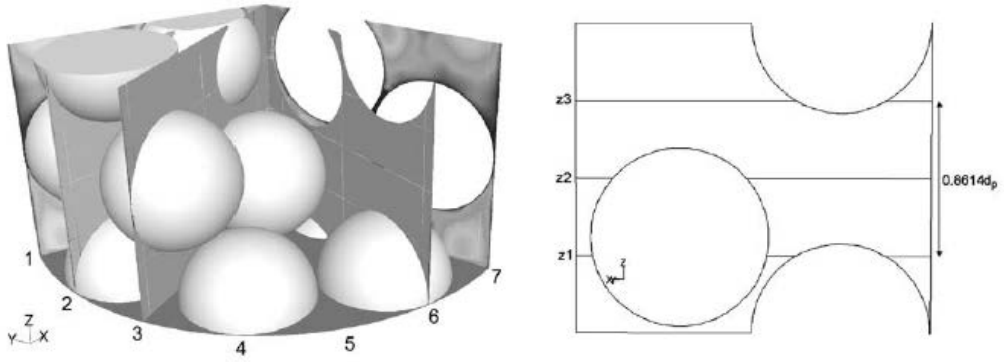


FIG. 10. Comparison section with seven tangential planes and axial profile lines indicated.

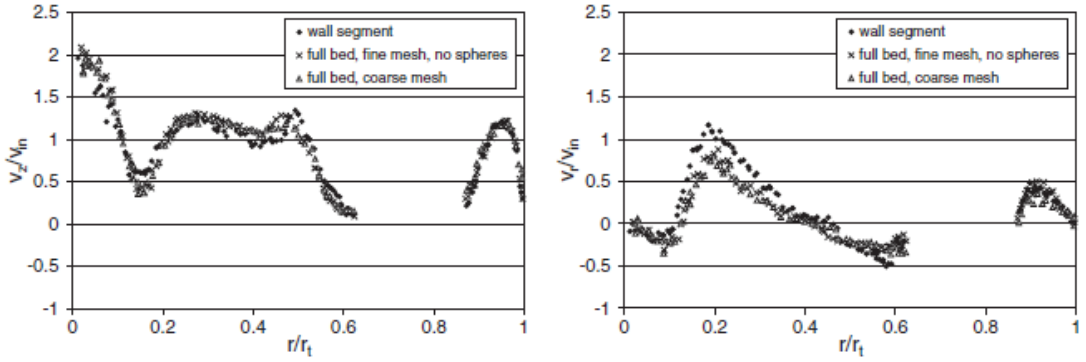
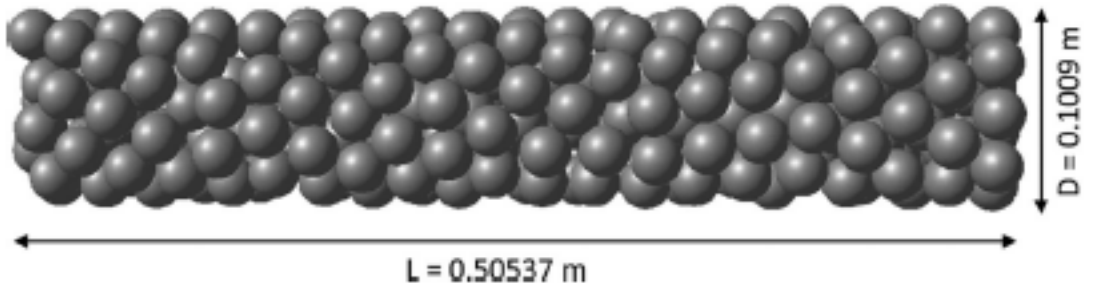


FIG. 11. Full-bed and WS mesh comparisons of axial and radial velocity components (at Z3).

Dixon AG, Nijemeisland M, Stitt EH. Packed Tubular Reactor Modeling and Catalyst Design using Computational Fluid Dynamics. In: Guy BM, ed. Advances in Chemical Engineering. Vol Volume 31: Academic Press; 2006:307-389.



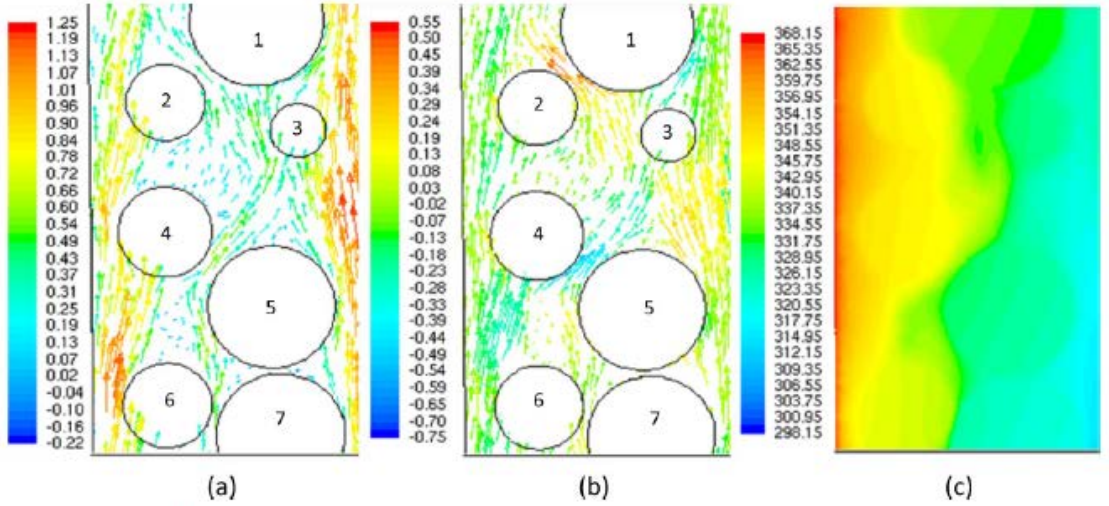


Figure 9. Close-up analysis of boxed regions from Figure 8 with $N = 3.96$ and $Re = 240$: (a) velocity vectors colored by axial velocity (m/s), (b) velocity vectors colored by radial velocity (m/s), and (c) temperature contours (K).

Behnam M, Dixon AG, Nijemeisland M, Stitt EH. A New Approach to Fixed Bed Radial Heat Transfer Modeling Using Velocity Fields from Computational Fluid Dynamics Simulations. *Ind Eng Chem Res.* 2013/11/06 2013;52(44):15244-1526

Principle Equations in 1-D Model

$$\frac{\partial c}{\partial t}+\left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial \bar{q}}{\partial t}-D_L\frac{\partial^2 c}{\partial x^2}=-\frac{\partial \upsilon_i c}{\partial x}$$

$$\frac{\partial \bar{q}}{\partial t}=k_n(q^*-\bar{q})$$

$$\varepsilon a_f\rho_f c_{pf}\frac{\partial T_f}{\partial t}-\varepsilon a_f k_{eff}\frac{\partial^2 T_f}{\partial x^2}=-\varepsilon a_f\rho_f\upsilon_i c_{pf}\frac{\partial T_f}{\partial x}+a_f a_s h_s\left(T_s-T_f\right)+P_i h_i\left(T_w-T_f\right)$$

$$(1-\varepsilon)\rho_s c_{ps}\frac{\partial T_s}{\partial t}=a_f a_s h_s\left(T_f-T_s\right)-(1-\varepsilon)a_f\lambda\frac{\partial q}{\partial t}$$

$$a_w\rho_w c_{pw}\frac{\partial T_w}{\partial t}-a_w k_w\frac{\partial^2 T_w}{\partial x^2}=p_i h_i\left(T_f-T_w\right)+P_o h_o\left(T_a-T_w\right)$$

$$n=\frac{ap}{\left[1+(bp)^t\right]^{1/t}};\qquad b=b_0\exp(E/T);\qquad a=a_0\exp(E/T);\qquad t=t_0+c/T$$

$$\frac{1}{Pe}=\frac{20}{\varepsilon}\left(\frac{D}{2\upsilon R_p}\right)+\frac{1}{2}=\frac{20}{ReSc}+\frac{1}{2}$$

$$\frac{1}{Pe}=\frac{0.73\varepsilon}{ReSc}+\frac{1}{2\left(1+\frac{13\cdot 0.73\varepsilon}{ReSc}\right)}\qquad 0.0377<2R_p<0.607\ \text{cm}$$

$$h_i=\frac{k_f}{2R_i}Nu\quad\text{with}\quad Nu=2.03Re^{0.8}\exp\left(-6\frac{R_p}{R_i}\right)$$

$$c_p=a_o+a_1T_f+a_2T_f^{\,2}+a_3T_f^{\,3}$$

$$Sh=2+1.1Sc^{\frac{1}{3}}Re^{0.6}\qquad h_s=\frac{ShD}{2R_p}$$

$$k_e=k_f\left(\frac{k_s}{k_f}\right)^n\quad\text{with}\quad n=0.280-0.757\log_{10}\varepsilon-0.057\log_{10}\left(\frac{k_s}{k_f}\right)$$

$$k_{eff}=k_f\left(\frac{k_e}{k_f}+0.75PrRe\right)\quad\text{where}\quad Pr=\frac{c_p\mu}{\rho_f k_f}$$

All variables in Mass and Heat Balance Equations are determined except D_L, k_n, *and* h_o

Virtual Adsorption Test Suite

- Matlab/COMSOL Component:
  - Inputs engineering data from actual or proposed test (breakthrough or cyclic)
  - Based on inlet conditions, calculates gas properties required for heat and mass transfer correlations
  - Builds requested PDE-based model with specified grid spacing, time steps, cycles etc.
  - Hands off model to COMSOL Multiphysics (used as PDE Solver) for execution and retrieves results when complete
  - Has been used with NASA X-TOOLSS (genetic algorithms) for parameter optimization
  - Allows for multi-variable parametric runs, and compares SSR of results vs. test data for parameter optimization
  - Generates paper-ready plots including plot over of test data
- Mathcad Component:
  - Provides independent verification of all calculations in Matlab component
  - Provides sensitivity analysis of correlations to temperature and concentration changes expected during a simulation

Centerline LDF fits database.

File Record Calculations COMSOL

General Information

Record Number 5

Description	Centerline Fitting
Data Source	MSMBT Test on 04-07-94M
Sorbent Type	Grace Davison 5A Grade 5
Test Stand	MSMBT Cylindrical Columi
Run Identifier	W-F LDF after fit to center
Notes	
Observations	
Standard Temp[degC]	0
Standard Press[kPa]	101.325

Adsorption Conditions

Ads Flow Rate[slpm]	28.26
Ads Initial Temp[degC]	23.35
Ads Inlet Temp[degC]	22.35
Constant or Timelined	Constant
CO2/H2O/O2/N2[kPa]	0 0.805 0 107.24
Constant or Timelined	Constant
Ads Inlet Air[kPa]	0
Ads Inlet He[kPa]	0
Ads Sorbate	H2O
Ads Initial Conc[mol/m^3]	0.001
Ads Initial Load[mol/m^3]	1
Sorbate MolWt[kg/mol]	

Desorption Conditions

Des Flow Rate[l/min]	28.04
Des Initial Temp[degC]	22.406
Constant or Timelined	Constant
Des Inlet Temp[degC]	22.406
CO2/H2O/O2/N2[kPa]	0 0.805 0 106.064
Constant or Timelined	Constant
Des Inlet Air[kPa]	0
Des Inlet He[kPa]	0
Des Sorbate	H2O
Des Initial Conc[mol/m^3]	0.001
Des Initial Load[mol/m^3]	1

Canister Information

Free Flow Area[cm^2]	17.814
Canister CS Area[cm^2]	2.45
Can Inner Perimeter[cm]	14.96
Can Outer Perimeter[cm]	15.96
Bed Length[m]	0.254
Void Fraction	0.33
Wall Void Fraction	1
Can Cond[W/(m*K)]	16.8
Can Q Capac[J/(kg*K)]	475
Can Density[kg/m^3]	7833
Ambient Temp[degC]	22.406
Can-Amb H[W/(m^2*K)]	1.685

Sorbent Information

Sorbent Type	5A
Sorbent Mass[g]	0
Part Density[kg/m^3]	1180
Pellet Diameter[mm]	2.32
Pellet Length[mm]	0
Mass Trans Coeff[1/s]	0.00098
Sorb Q Cond[W/(m*K)]	0.12
Sorb Q Capac[J/(kg*K)]	1046.7
Heat of Ads[kJ/mol]	-65.1

Inlet Temperature / Error Checking

Constant or Timelined	Timelined
Timeline File Name	Templn.txt
Conc Test Data File	Conc 975 1000 SSE.txt
Gas Temp Test Data File	GasTemp 500 975 SSE.tx
Col Temp Test Data File	none
Scope of Err Check[%]	75 101
Scaling for Err[fraction]	1 1 0.5 0.5 0.5 0.5 0.2 0.2

Simulation Control

Model Name/Solver	PDE FC
Half-Cycle Length[s]	36000
Number of Half Cycles	1
Time Step[s]	30
Node Sep Max[m]	0.001
Node Sep Init[m]	0.0001
Parametric Iterations	1
Parameter Name	AdsAxialDisp
Minimum Value	0.00238473
Maximum Value	0.001

Plot Specifications

Spatial Locations	200
Num of Plot Points	3 3 25 25 25 25 25
Plot Type	PlotOver
Plots per Page	2
Simulation Data	cWT TgWT ct
Conc Data File	Test Concs for Plots with I
Conc Legends	Inlet Mid Exit Mixed
Gas Temp Data	Test Temps for Plots with
Gas Temp Legends	Inlet Mid Exit
Col Temp Data	none
Col Temp Legends	none
y-axis high limit	1 2 1 1 1 2 1
y-axis low limit	1 2 1 1 1 2 1
Start/End Slope Max	25 100
Legend Location	none none none
ParaBox Location	none none none
Test Data OffSet[s]	0 0 0
Write Sim Data?	no

Adsorption Calculations

Ads Concentrat[mol/m^3]	0.327645
Ads Interstitial Vel[m/s]	0.812856
Ads Bed Loading[mol/kg]	13.0163
Ads Residence Time[s]	0.312478
Ads Stoichio BT Time[m]	495.674

Adsorption Gas Properties

Ads Viscosity[uPa*s]	17.5667
Ads Mol Diff[m^2/s]	2.379e-05
Ads Reynolds Number	43.5252
Ads Schmidt Number	0.601007
Gas Q Cap[kJ/(kg*K)]	1.048
Axial Cond[W/(m*K)]	0.671489
Sorbate Q Cap[kJ/(kg*K)]	1.89756
Sorb-Gas H[W/(m^2*K)]	144.334
Gas-Can H[W/(m^2*K)]	19.9474

Adsorption Mass Transfer

Ads Axial Disp[m^2/s]	0.0023847
Ads Axial Dis Mn[m^2/s]	0.000844941
Ads Axial Dis Mx[m^2/s]	0.00238473
Ads Film Diff[m/s]	0.112096
Ads Film Diff Min[m/s]	0.104927
Ads Film Diff Max[m/s]	0.114299

Adsorption Miscellaneous

Ads Total Press[kPa]	108.045
Ads Mix Mol Wt[g/mole]	27.9385
Ads Gas Dens[kg/m^3]	1.22861
Ads Superfic Vel[m/s]	0.268243
Ads Solid Conc[mol/m^3]	15359.3

Calculations

Equil Work Cap[mol/kg]	0.0042
Equiv Pellet Dia[mm]	2.32
Area to Vol ratio[1/m]	192.529
Void from Sorb Mass	0
Packed Dens[kg/m^3]	790.6
Sorb Mass via Void[g]	357.727
Sim - Test Error	35.5539
Calculated Offset[s]	-1220.3371 -4957.7211

Desorption Calculations

Des Concentrat[mol/m^3]	0.327583
Des Interstitial Vel[m/s]	0.815558
Des Bed Loading[mol/kg]	13.0121
Des Residence Time[s]	0.311443
Des Stoichio BT Time[m]	493.966

Desorption Gas Properties

Des Viscosity[uPa*s]	17.5679
Des Mol Diff[m^2/s]	2.40598e-05
Des Reynolds Number	43.1821
Des Schmidt Number	0.60098
Gas Q Cap[kJ/(mol*K)]	1.04806
Axial Cond[W/(m*K)]	0.666838
Sorbate Q Cap[J/(kg*K)]	1.8976
Sorb-Gas H[W/(m^2*K)]	143.799
Gas-Can H[W/(m^2*K)]	19.8251

Desorption Mass Transfer

Des Axial Disp[m^2/s]	0.00086174
Des Axial Dis Mn[m^2/s]	0.000847087
Des Axial Dis Mx[m^2/s]	0.00240422
Des Film Diff[1/s]	0.112927
Des Film Diff Min[1/s]	0.105579
Des Film Diff Max[1/s]	0.115595

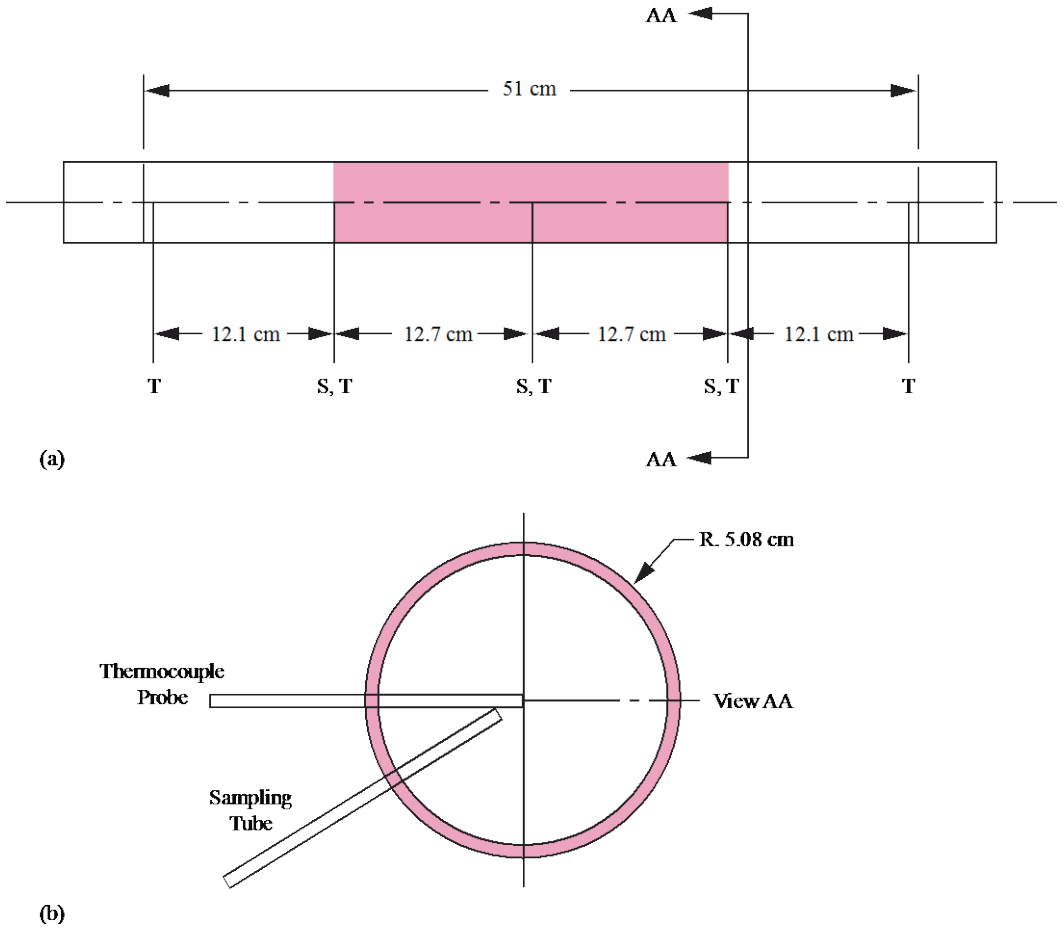
Desorption Miscellaneous

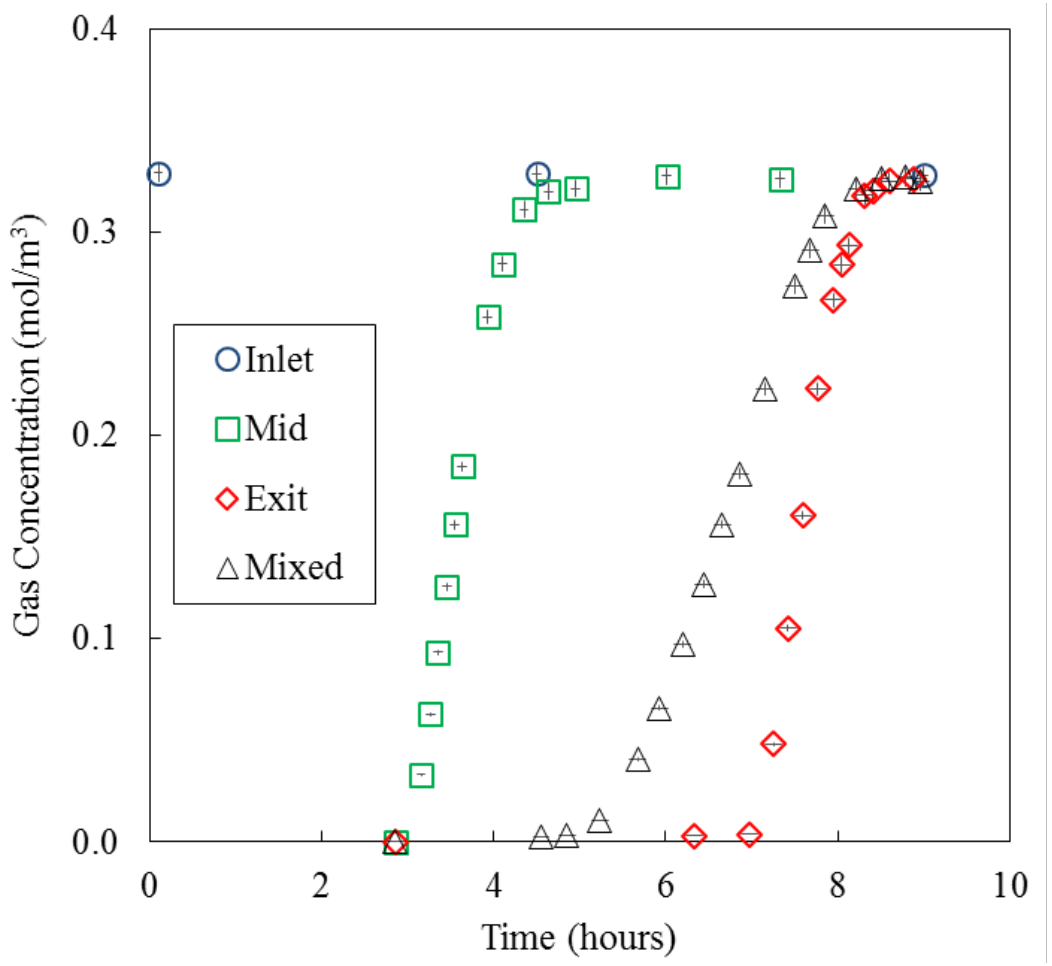
Des Total Press[kPa]	106.869
Des Mix Mol Wt[g/mole]	27.9377
Des Gas Dens[kg/m^3]	1.21498
Des Superfic Vel[m/s]	0.269134
Des Solid Conc[mol/m^3]	15354.3

Toth Isotherm Parameters

Toth a0[mol/kg/kPa]	1.106e-08
Toth b0[1/kPa]	4.714e-10
Toth E[K]	9955
Toth to	0.3548
Toth c[K]	-51.14

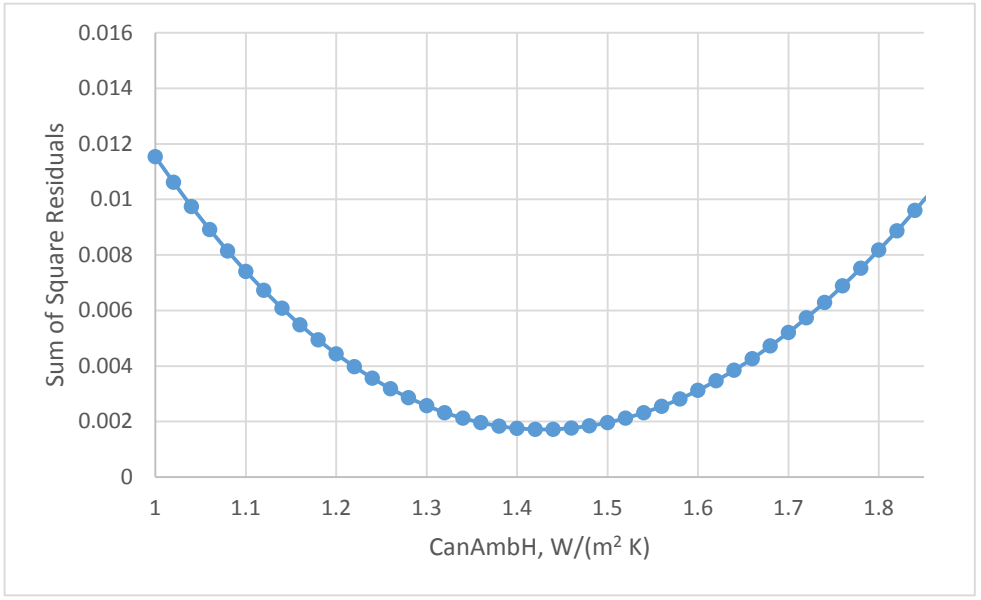
Experimental Results for H_2O on 5A

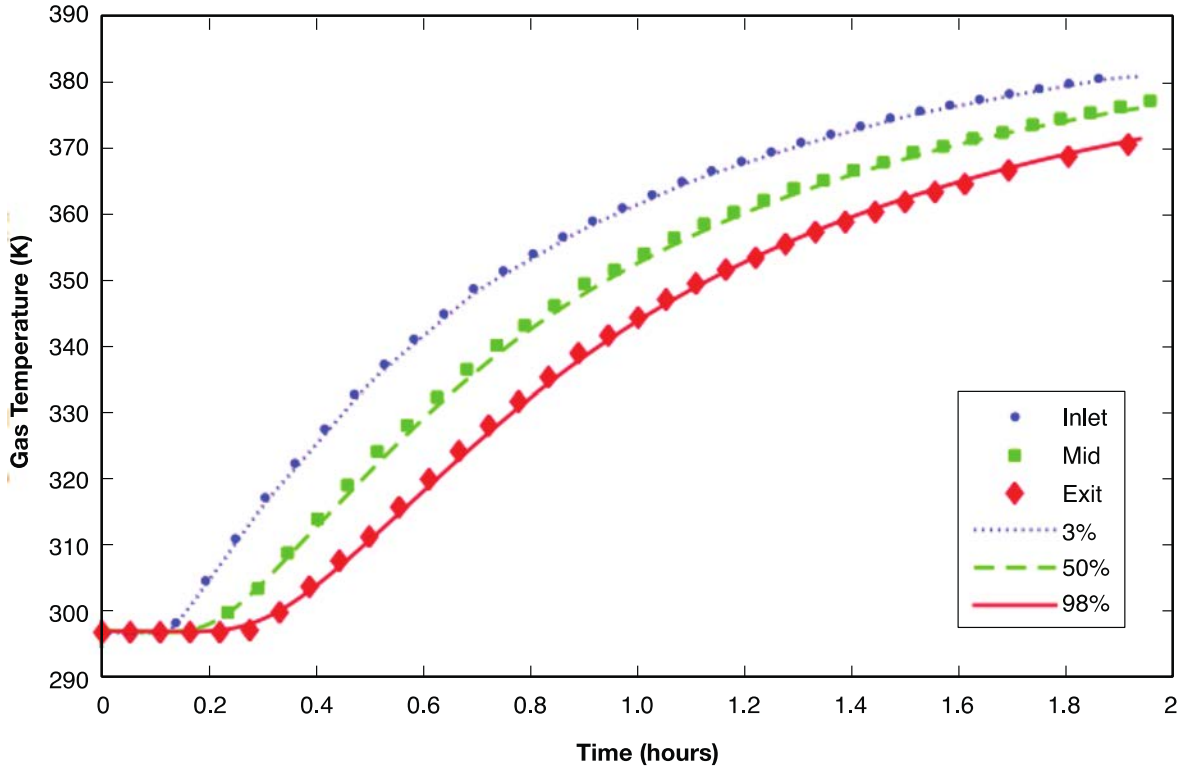




How to independently derive free parameters?

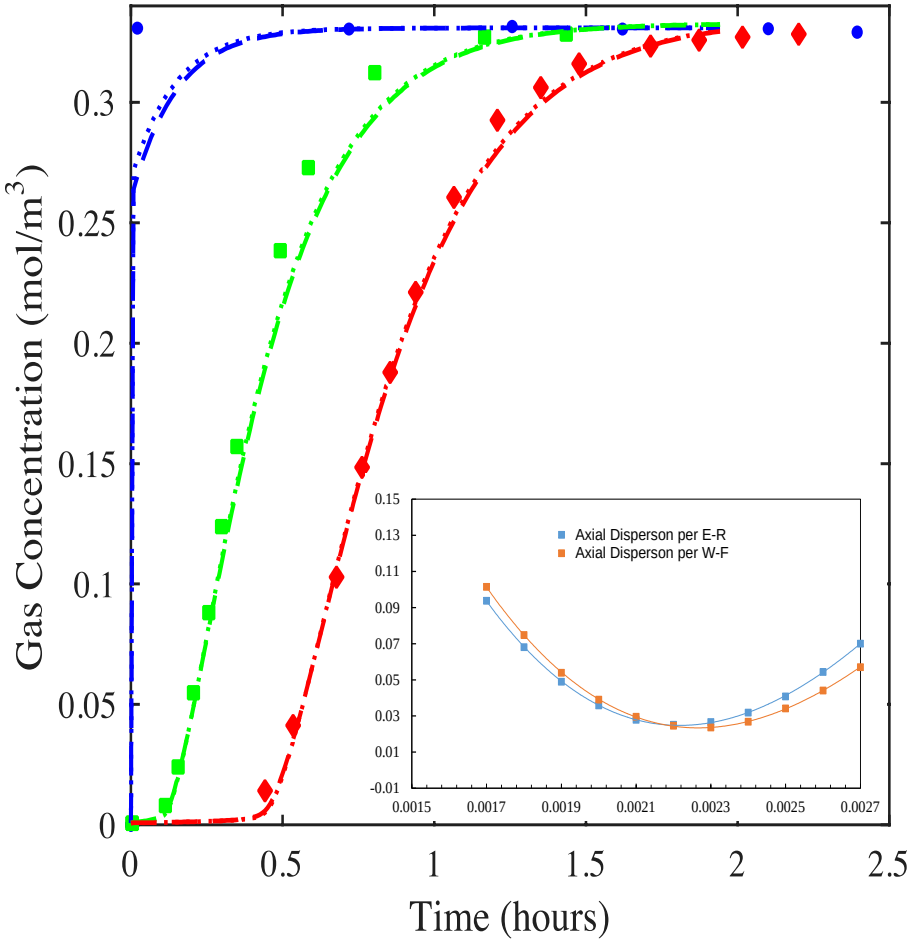
Step 1: Wall to Ambient Heat Transfer Coefficient

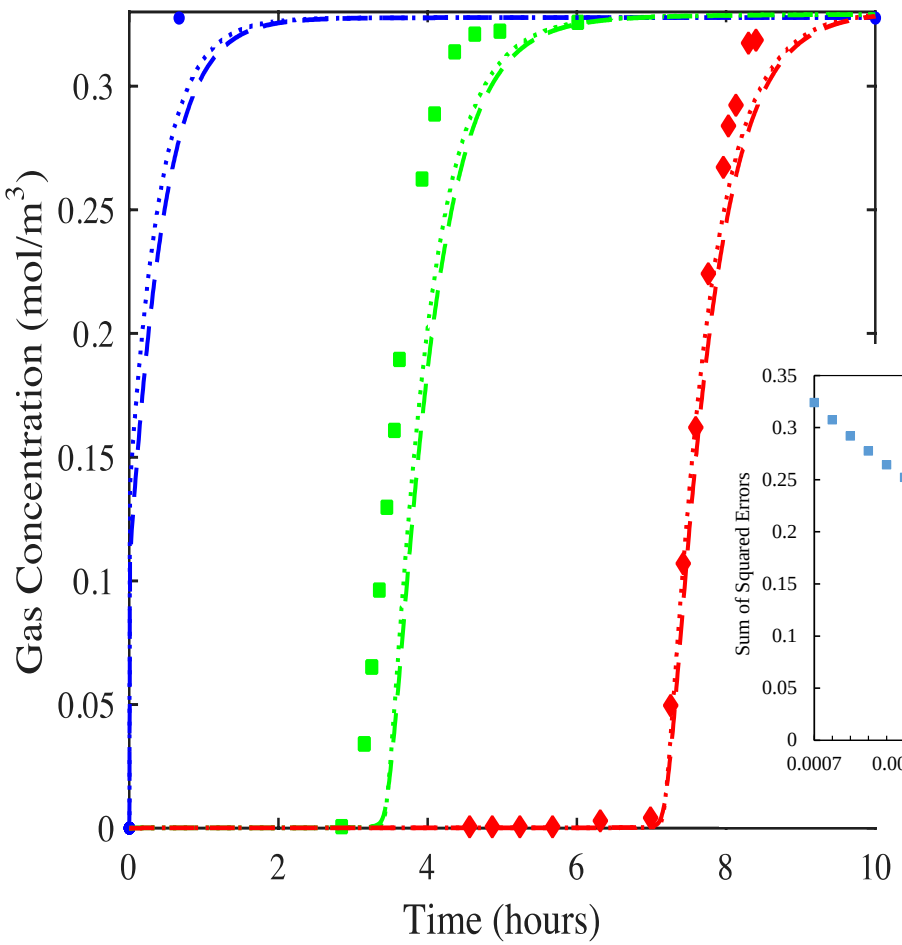




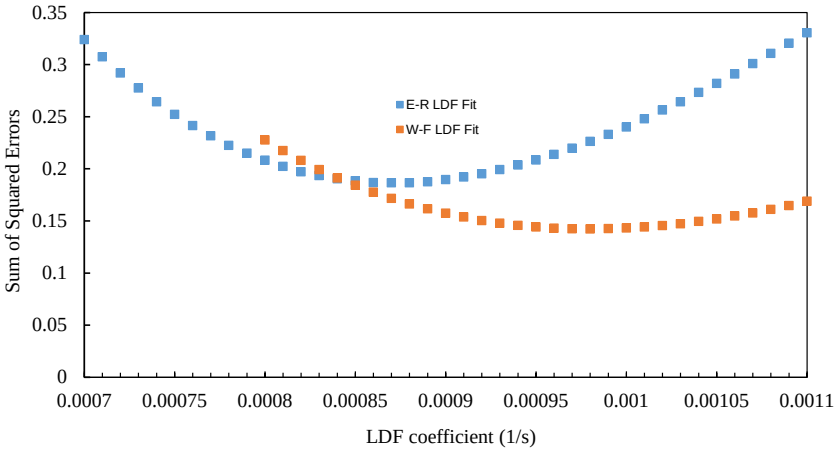
h_o is empirically derived via a Thermal Characterization Test

Step 2: Linear Driving Force Mass Transfer Coefficient





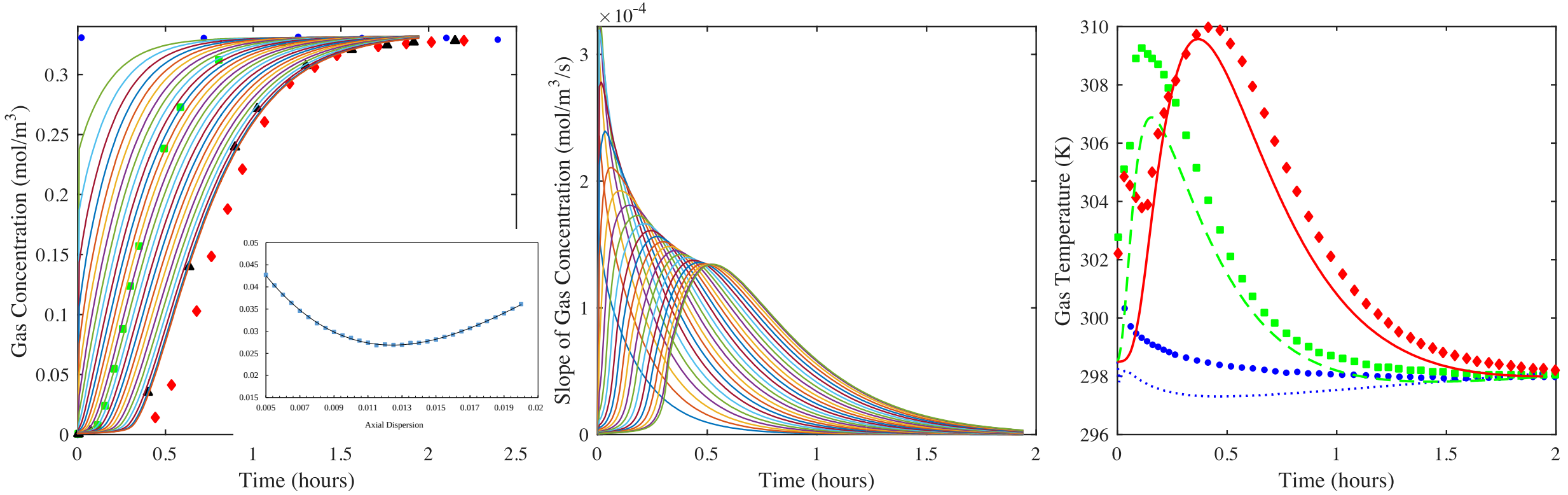
Diamonds: experimental data; dashed lines: simulations with the Edwards and Richardson correlation for axial dispersion and corresponding k_n values; dotted lines: simulations with the Wakao and Funazkri correlation for axial dispersion and corresponding k_n values.



Fits of the 1-D axial dispersed plug flow model to the 97.5% location (diamonds) experimental centerline gas-phase concentration breakthrough curves for CO_2 (left) and H_2O vapor (right) on zeolite 5A, and corresponding predictions from the model of the 2.5% (circles) and 50% (squares) locations. The saturation term in the CO_2-zeolite 5A isotherm was increased by 15%. The saturation term in the H_2O vapor-zeolite 5A isotherm was decreased by 3%. **The void fraction was reduced to 0.33 based on the Cheng distribution (Cheng *et al.*, 1991) with C = 1.4 and N = 5, as recommended by Nield and Bejan (1992)**

k_n is empirically derived via fitting to centerline concentration breakthough curve. For this step, dispersion is taken to result from pellet effects only (no wall effects). Choice of dispersion correlation has a small impact on k_n

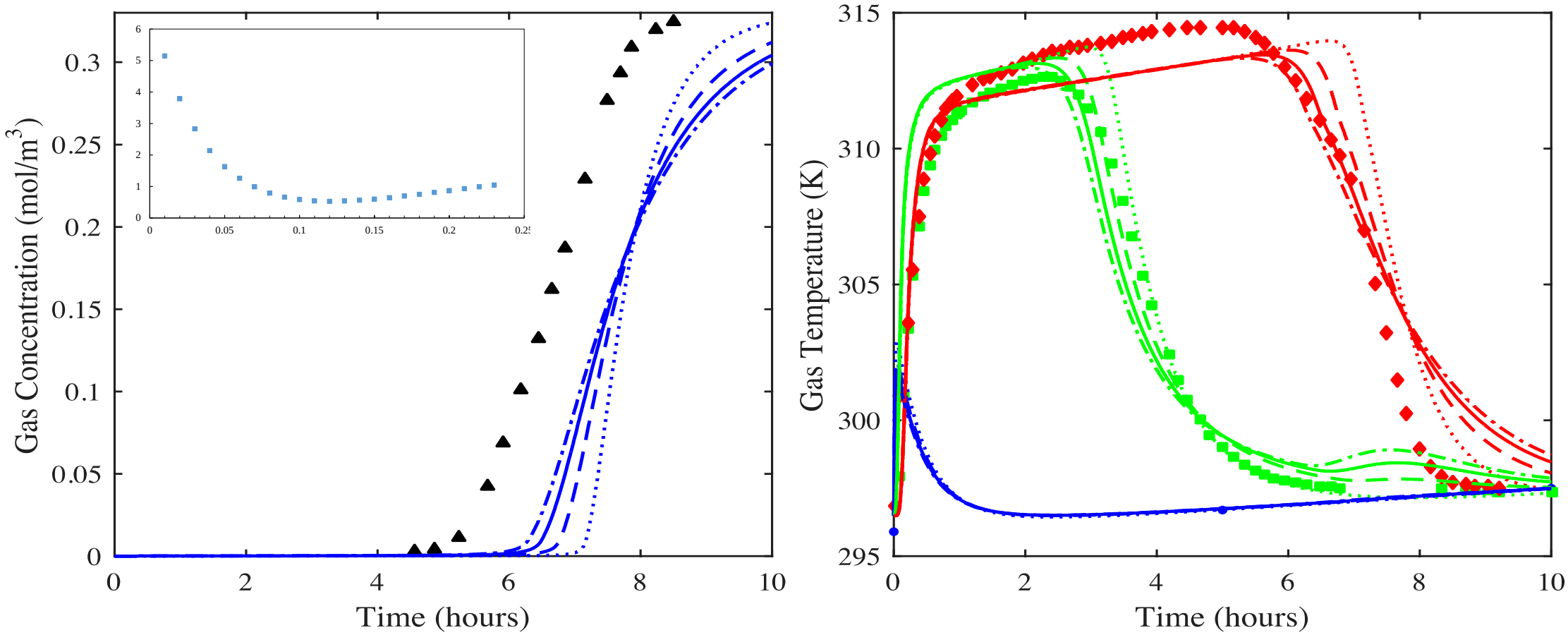
Step 3: Axial Dispersion Coefficient (CO_2 Case)



CO_2 on zeolite 5A: Fit of the 1-D axial dispersed plug flow model to the outside bed (triangles) experimental breakthrough curve using a value of D_L 7 times greater than that from the Wakao and Funazkri correlation and the fitted LDF k_n = 0.0023 s^{-1} (left panel). The reported saturation term for the CO_2-zeolite 5A isotherm was used, along with **the reported void fraction of 0.35**. Predictions from the model (lines) of the gas-phase concentration breakthrough curves at 0, 4, 8, 12, …, 92, 96 and 100% locations in the bed are also shown in the left panel, along with the 2.5% (circles), 50% (squares) and 97.5% location (diamonds) experimental center line gas-phase concentration breakthrough curves (left panel). The corresponding derivative (or slope) of the predicted gas-phase concentration breakthrough curves in the bed are shown in the middle panel. Predictions from the model (lines) of the 2.5% (circles), 50% (squares) and 97.5% location (diamonds) experimental center line temperature profile histories are shown in the right panel.

D_L term is fit to mixed gas concentration (far downstream), but requires value 7 times the correlation value to compensate for wall channeling. Fit is specific to the size of the column; for a much larger column wall channeling may be neglected and correlated values of D_L used (but not for fixed beds with a tube to pellet ratio of 20 as in this case, or less)

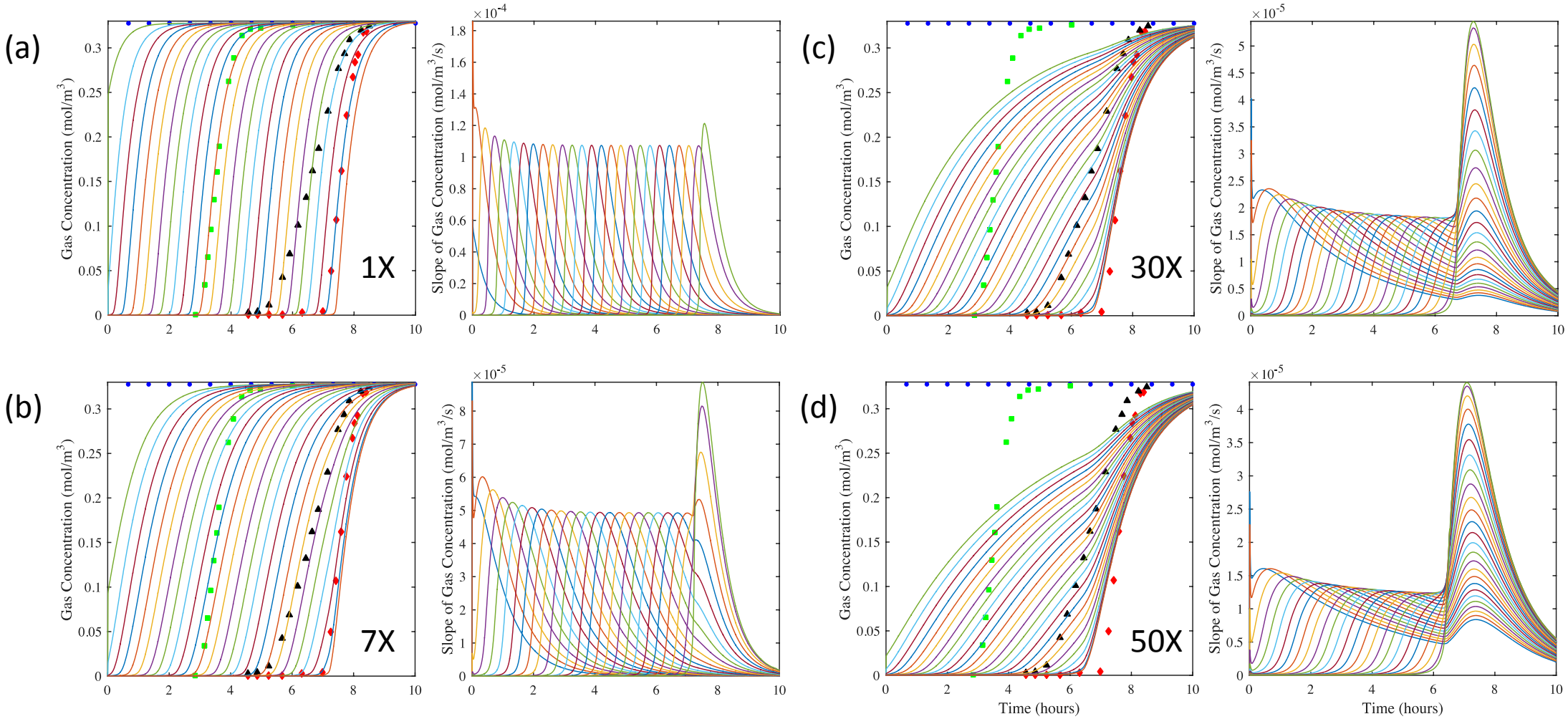
Step 3: Axial Dispersion Coefficient (H_2O Case)



H_2O vapor on zeolite 5A: Predictions from the 1-D axial dispersed plug flow model of the outside the bed (triangles) experimental breakthrough curve when varying the value of D_L. **D_L = 10 (dotted lines), 30 (dashed lines), 50 (solid lines) and 70 (dash-dot lines) times greater than Wakao and Funazkri correlation** with the LDF k_n = 0.00083 s^{-1} (left panel). The reported saturation term for the H_2O-zeolite 5A isotherm was used, along with the reported void fraction of 0.35. The corresponding predictions from the model (lines) of the 2.5% (circles), 50% (squares) and 97.5% location (diamonds) experimental center line temperature profile histories are shown in the right panel.

D_L term is fit to mixed gas concentration (far downstream), but requires value ***50(!)*** times the correlation value to compensate for wall channeling. However the temperature profiles deviate increasingly from the test data with increasing D_L indicating a breakdown of the axial dispersed plug flow model.

Breakthrough Sharpening and Breakdown of Constant Pattern Behavior



H_2O vapor on zeolite 5A: Predictions from the model (lines) shown in Figure 9 of the gas-phase concentration breakthrough curves at 0, 4, 8, 12, …, 92, 96 and 100% locations in the bed (left panels). The 2.5% (circles), 50% (squares) and 97.5% location (diamonds) experimental centerline gas-phase concentration breakthrough curves are also shown for comparison in the left panels. The corresponding derivatives (or slopes) of the gas-phase concentration breakthrough curves in the bed are shown in the right panels. (a) D_L = Wakao-Funazkri correlation, and (b) D_L = 7, (c) 30 and (d) 50 times greater than Wakao and Funazkri correlation.

At 7X, internal concentration history slope matches mixed concentration just as for CO2 case. This indicates that same dispersive mechanism occurs regardless of sorbate. To overcome non-physical breakthrough sharpening, D_L must be increased by 50X to decrease breakthrough slope. Expected CPB is lost entirely for this condition.

Conclusions

- Breakthrough tests with tube diameter to pellet diameter ratios of around 20 (or less), are subject to wall channeling, an mechanism not captured in standard dispersive correlations. *Breakthrough tests are generally subscale to conserve sorbent materials and gas flow equipment costs and thus frequently in this range.*
- The typical breakthrough measurement is taken far downstream, after mixing. *Fitting the mass transfer coefficient to this measurement will provide erroneous results for a larger (or smaller) diameter column due to the influence of channeling.*
- A method has been demonstrated where a centerline measurement is used to derive a mass transfer coefficient that captures physics free of wall effects and thus appropriate for scale-up to large diameter columns.
- Using the mass transfer coefficient derived above, this method uses the mixed concentration data for fitting of a dispersion coefficient D_L specific to the tube diameter, as needed for processes that utilize small diameter tubes.

Conclusions (continued)

- However fitting D_L blindly to the breakthrough curve (as apparent in many published breakthrough analyses) can, in specific cases, result in a complete breakdown of the axially dispersed plug flow model, and result in fitted coefficients that are incorrect.
- The axially dispersed plug flow equation and the Danckwerts boundary condition works well for values of dispersion within bounds of accepted correlations
- However, for specific combinations of $K_{d,}$ D_L and k_n this model breaks down due to the elimination of dispersion at the outlet boundary. In these cases, significant breakthrough sharpening occurs as well as distortion of the internal concentration, deviating from the accepted CPB for these systems.